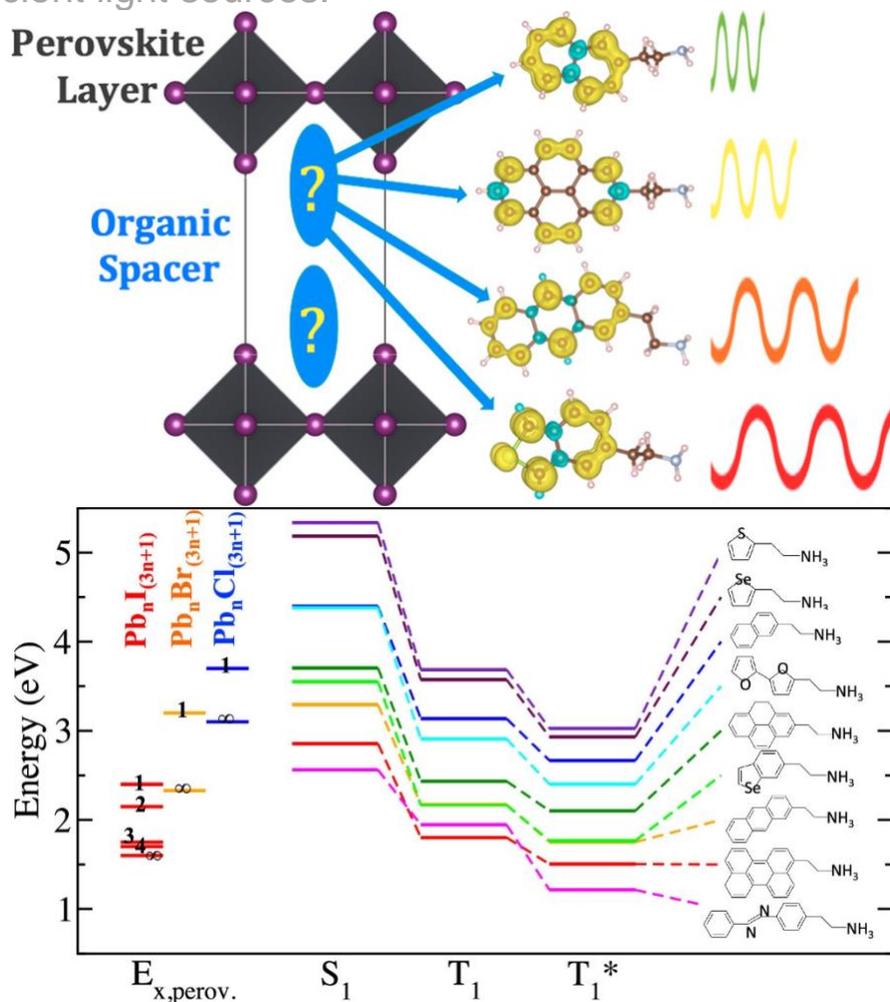


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Tuning electronic Structure in Layered Perovskites with Organic Spacer Substitution

This work's computational predictions demonstrate that the electronic structure of 2D layered hybrid metal-halide organic perovskites (LHOPs) paired with conjugated organic spacers is extremely tunable, which suggests broad variability and control over dynamics of energy and charge carriers. In particular, light-emitting applications involving LHOPs is a promising field of research and should be further investigated to discover potential next generation, wavelength tuned, highly efficient light sources.



Top: Example of how different organic spacers within the perovskite structure could emit different colored light. Bottom: An exact diagram of the alignment between perovskite exciton levels, organic triplet T_1 excitation energies, and organic T_1^* excited-state geometry emission energies for a select subset of examined organic spacers.

The Science

Los Alamos National Laboratory collaborates with the University of Illinois at Urbana-Champaign, Rice University, and scientists at Univ. Rennes to utilize time-dependent density functional theory in order to predict optically tunable pairings of 2D LHOPs with conjugated organic spacers for light emission applications. First singlet and triplet excitation energies were calculated in the ground state geometry and then the first triplet excitation energy in the excite-triplet-state relaxed geometry. These energies were compared to the known exciton energy levels of Pb_nX_{3n+1} perovskite layers ($X = I, Br, C$). We carefully verified that our predictions remained consistent when tail geometries are changed and the organic spacers are placed into their LHOP cluster geometries. Molecular dynamics is used to demonstrate that finite temperatures and the perovskite environment have little influence on the average excitation energies. However we do find significant thermal broadening of up to 0.5 eV of the optical excitation energies appearing due to finite temperature effects.

The Impact

Electronic structure calculations are used to predict multiple viable pairings of organic spacer candidates with single perovskite layers, to facilitate design of LHOPs with desired energy level alignments. These pairings may achieve potential triplet emission across the visible spectral range. In particular, light emitting applications involving LHOPs is a promising field of research and should be investigated to discover potential next generation, wavelength tuned, highly efficient light sources.

Summary

We successfully identify ten organic spacer candidates for possible pairing with perovskite layers of specific halide composition to achieve triplet light emission across the visible energy range and offer potential solutions for tuned light emission applications. We verified that our predictions remain consistent even tail geometries are altered and the organic candidates are placed into their clustered LHOP geometries. Finally, finite temperature dynamics of organic spacers in the perovskite crystal, as simulated by ab initio molecular dynamics, result in a broadening of excitation energies slightly below the results obtained for isolated geometries. This thermal broadening of the excitation energies provides an important consideration for future theoretical and experimental work designing light emitting LHOP devices. Our computational predictions demonstrate that the electronic structure of LHOPs paired with conjugated organic spacers is

extremely tunable, suggesting broad variability and control over the dynamics of energy and charge carriers.

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Publications

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